

WORK DONE IN 1954 BY INSTITUTES OF THE DEPARTMENT OF CHEMICAL SCIENCES,

ACADEMY OF SCIENCES USSR

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M. M. Dubinin, Academician-Secretary of the Department of Chemical Sciences, Academy of Sciences USSR, presented at a general meeting of the department a report dealing with the general results of the work carried out by the institutes of the department during 1954.

Substantially the institutes of the department had concentrated on the solution of cardinal theoretical problems in the field of chemistry, which have an important bearing on the development of scientific methods to be applied with the purpose of advancing further the people's economy. M. M. Dubinin outlined as follows the most significant results achieved along these lines in 1954.

As far as development of a scientific basis for heterogeneous catalysis is concerned, significant results have been obtained both in the theoretical field (by developing the multiplet theory further) and the practical field (in work on individual catalytic processes which are of practical importance). Data have been obtained on the structure, relative activity, and selectivity of the action of oxides, sulfides, and selenides of zinc, nickel, and chromium from the standpoint of their application in the decomposition of isopropyl alcohol, hydration [hydrogenation?] of butadiene, and reduction of nitrobenzene. These data lead to the conclusion that the atoms of the nonmetallic elements participate in the formation of active centers and of multiplet complexes.

Electronic concepts of catalysis have been developed. A quantum-mechanical analysis of the effects exerted by admixtures contained in the volume of semiconductor crystals on the concentration of the electron-hole gas on the surface of the crystals was carried out for the first time. It was shown that the dimensions of the crystals are the decisive factor: as the crystals increase in size, the effect exerted by the admixtures gradually increases.

In the field of petroleum chemistry a new and important reaction of the cyclization of paraffin hydrocarbons with the formation of a five-membered ring was discovered. This reaction opens up perspectives of utilizing hydrocarbon crude materials and throws new light on the formation of cyclic hydrocarbons contained in crude petroleum.

Together with the Commission on Spectroscopy at the Department of Physicomathematical Sciences, a method of analysis was developed by means of which closely defined groups of aromatic hydrocarbons contained in ligroin can be determined. This method makes it possible to determine the content of benzene homologs substituted to a varying extent, to establish the position of side chains, and to determine the content of cyclohexane homologs after the latter have been transformed into benzene derivatives.

A considerable amount of work which led to the formulation of general relationships has been carried out on the tautomerism of organoelemental compounds. It has been shown that whenever substances which exhibit tautomerism or do not exhibit tautomerism react in a dual manner, this duality is always due to the presence of a system of conjugated bonds which enables the substances to react either at the 1-2 bonds or the 1-4 bonds. It follows from this that tautomerism is only a particular case of the manifestation of the dual reactive capacity



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with which all compounds that have conjugated bonds are endowed. On the basis of investigations in this field, a systematization of the types of conjugation was proposed and the pnenomenon of dual reactivity was considered from the standpoint of its relationship to orientation phenomena in the substitution of aromatic nuclei.

In research on the kinetics and mechanism of chemical reactions, certain concepts were developed of the special role played by the initial period in chain oxidation reactions which take place in the presence of initiating admixtures. The accuracy of these concepts was confirmed by experimental results. It was established that when the catalyst is removed after completion of the original, initiating stage of the reaction, frequently no further influence on the course of the process is exerted thereby.

The use of tracer atoms in research on the mechanism of chemical reactions was expanded for the purpose of clarifying the behavior of intermediate products and their role in the total chemical reaction.

New experimental data have been obtained in theoretical work on the combustion of gases. These data can be of substantial help in the development of practical measures for preventing ignition of gas and gas fires in coal mines.

In research on high molecular compounds . Was established that the high temperature of softening and low solubility of polyamides are due to the great number of hydrogen bonds between the polyamide molecules. When the number of hydrogen bonds is reduced (for instance, by synthesizing mixed polyamides), the temperature of softening of the polymer is lowered and its solubility increased. It has been established that the characteristics of polyamides and of polyesters depend both on the number of carbon atoms in the chain of the initial products [monomers] and on whether this number is even or odd.

The molecular-statistic theory of the structure of polymer chains has been expanded. A theoretical treatment of the behavior of chains at high degrees of stretching has shown that energy effects arise in stretching. Methods have been developed for calculating the dipole moments of polymer chains and estimating their optical anisotropy on the basis of the chemical structure and stretching. The results that have been obtained represent significant progress in the theory which aims to establish a direct connection between mechanical properties of polymers and their chemical structure.

Systematic investigations in the field of emulsion copolymerization made it possible to use technically accessible monomers for the preparation of a new synthetic rubber which has valuable properties.

The reaction of the formation of polysulfide sulfur under the effect of free radicals has been studied in relevant experiments. This work has added to the knowledge of the formation of monosulfide and polysulfide links in the process of vulcanization with sulfur.

In the field of drug synthesis, laboratory experiments have been completed on the preparation and physiological properties of isopromedol, which is a much more effective analgesic than promedol.

Work on adsorption phenomena, which was carried out with the use of extensive experimental data, led to substantiation of the concept in regard to the polymodal character of the distribution of activated carbon pore volumes with reference to the dimensions of these pores. On the basis of detailed determinations of isotherms and heats of adsorption carried out on porous and nonporous carbon adsorbents, theoretical concepts in regard to the mechanism of the adsorption of water vapor have been formulated.



The theoretical background of static and dynamic ion-exchange chromatography of large organic ions on synthetic ion-exchange resins has been formulated. The structure which ion-exchange resins must have has been established and a method of synthesizing them has been developed which eliminates the capture of large organic ions by the resins when these ions are eluted with acids.

Application of the method of tracer atoms in the study of adsorption phenomena made it possible to obtain new data on the structure of the double electric layer. It was shown that in addition to phenomena resulting in purely electrostatic adsorption, chemical factors are effective in bringing about adsorption of ions on metal surfaces.

Some investigations in the field of chemical generation of electric currents were carried out with the purpose of increasing the capacity of storage batteries and prolonging their useful life. The mechanism of the functioning of the active mass of the lead electrodes was established. The zero point of lead dioxide in sulfuric acid was determined for the first time and a theory of the sulfation of the electrodes was developed.

On the basis of investigations in regard to the influence exerted by the composition and structure of magnesium alloys on their corrosion stability and effectiveness as protectors, recommendations have been made pertaining to the use of these alloys for the protection of trestles of off-shore petroleum wells and of marine vessels. It has been shown for the first time that when an alloy is in the passive state the presence of cathodic ingredients increases its corrosion resistance. The relationships which have been established indicate ways of developing new corrosion-resistant alloys and particularly of increasing the corrosion resistance of stainless steels.

New and highly efficient methods of evaluating the lubricating properties of the media used in the working of metals by cutting or by applying pressure have been developed. These methods assure an effective selection of lubricating and cooling liquids adapted to the nature of the metal and to the type of deformation being applied. A number of new lubricating compositions has already been introduced into practical use on the basis of this work.

Geochemical investigations have been considerably expanded, particularly as far as the determination of the age of rock occurrences is concerned. The uranium-lead, potassium-argon, strontium, ionium, and radiocarbon method have been applied in these determinations. A systematic determination of the absolute age of geological objects in various parts of the USSR was begun in 1954.

Investigations on the geochemistry of sedimentary rocks have also been expanded. In particular, the collation of data on the geochemistry of carbonate deposits of the Russian platform has been completed. This work involved the drawing up of geochemical charts and of general schemes of the evolution of carbonate rocks of this region as far as their chemical composition is concerned. Investigations on the geochemistry of individual elements and on the geochemistry of rare earths had the purpose of establishing the relative content of rare-earth elements in monazites of various origin. It has been shown that the rare-earth element composition of monazites derived from pegmatites differs from a corresponding composition of accessory monazites derived from granites with which these monazites are associated. This conclusion confirms the assumption on the subject which was made at one time by Academician V. I. Vernadskiy.



In the field of analytical chemistry spectroscepic and chemical methods have been developed which are being applied in the determination of very small quantities of impurities present in a number of metals (germanium, zirconium, titanium, etc). Among the procedures developed, the method of radioactivation analysis deserves particular attention. A number of highly sensitive methods of polarographic analysis has also been developed. Together with workers at an electric lamp factory, a new model of a Soviet polarograph has been designed and constructed.

Hydrochemical work dealt with the study of physicochemical processes of the interaction between natural waters and the subsoil or rocks. On the basis of extensive experimental material, a characterization was given for the first time to water-imbibing rocks as compared with water derived from drill holes or wells. The principal characteristics typical for the formation of the composition of subterranean waters in the region where the Staling of Hydroelectric Station is located have been clarified.

In research on complex compounds, new methods have been used, i.e., the refractometric method, infrared absorption spectroscopy, and ultraviolet spectroscopy at low temperatures.

Using the laws underlying the trans-effect, a number of new complex compounds of platinum metals could be synthesized. A number of new compounds of rare elements was also synthesized and the most important physicochemical properties of these compounds were studied. The results that have been obtained are of importance from the standpoint of analytical applications and technological work on the production of the elements in question.

As a result of the investigation at high temperatures and high water-vapor pressures of phase equilibria in aqueous systems containing chlorides, sulfides of sodium, and sodium hydroxide, scientific data have been obtained which have a bearing on the deposition of solid salts in steam boilers operating at high pressures and superhigh pressures and also are of help in characterizing the phase composition of salts deposited in parts of high-pressure turbines which are exposed to the action of flow. These data are of importance for an understanding of the physicochemical processes which take place within boilers.

In the field of silicate chemistry, investigations have been successfully completed which have the purpose of developing further the thermodynamic and molecular theory of seignettoelectric and antiseignettoelectric phenomena. A number of ceramic seignettoelectrics has been subjected to many-sided investigation. The work on this subject marks a new stage in the progress of our knowledge on the subject of seignettoelectrics and is of considerable practical importance.

On the basis of investigations which established that the properties of clays change radically under the influence of additives, methods of using additives in connection with the processing of clay have been developed. This is a technique which is of great importance for the production of refractories, ceramic production, and other branches of the silicate industry.

The account given above represents a general outline of the most important work done at scientific institutions of the Department of Chemical Sciences. Of course, it does not by far give a complete picture of the activity of these institutions. After presenting this account, M. M. Dubinin dwelt on a number of shortcomings which became apparent in the work done within the department and mentioned the fields in which more research should be done.

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According to Dubinin, work which deals with structural theory and the theory of reactivity should be considerably expanded. In addition to older physical methods, it is necessary to apply extensively in this work such new methods of investigation as microwave spectroscopy, determination of paramagnetic resonance, and neutrongraphy of molecules. Dubinin mentioned in this connection that progress in work on the theory of structure has an important bearing on the development of general theoretical concepts in related fields of inorganic, organic, physical, and colloid chemistry, as well as on the solution of a number of problems of kinetics, catalysis, and the structure of high-molecular compounds.

Very serious tasks must be accomplished in the field of inorganic chemistry. One must first of all expand investigations in the chemistry of rare elements (particularly on the complex compounds of these elements), on the properties of highly purified metals, on methods for the analysis of impurities which are present in insignificant amounts, etc.

Increased stress should be laid on research in chemical thermodynamics and thermochemistry, particularly as far as heat capacities are concerned which lie within a broad range of temperatures and are necessary for the calculation of entropies and chemical equilibria. This work should be carried out first of all on systems which are of practical importance.

Equally important is the chemical and biological investigation of many types of natural compounds, work on which is on the borderline between organic chemistry, properly speaking, and biochemistry. The greatest attention should be paid to research in the chemistry of antibiotics, enzymes, hormones, and proteins.

After discussing briefly some completed investigations, the results of which are being introduced into practice or have already been introduced, Dubinin emphasized the importance of a close collaboration between scientists and industrialists for the most successful solution of problems that have a bearing on economic progress. Touching upon the problem of the training of personnel, he mentioned the necessity of considering the needs of specialties which lack personnel in distributing the aspirants among different specialties.

At the conclusion of his report, Dubinin expressed confidence that the contemplated reorganization of the department will have a beneficial effect on work in all of the most important fields. In connection with this, he discussed some future aspects of the activity of the department.

In 1954, a group of scientists of the department, together with scientists and prominent specialists from the ministries, defined the principal problems which determine the development of Soviet chemical science. Among these problems [subjects of investigation] are the theory of chemical structure and of reactivity, the scientific basis of the selection of catalysts, the development of new sources of electrical energy, the scientific basis of the production of new synthetic rubbers, plastics, synthetic fibers, and artificial leather, the synthesis of natural and [other] biologically important substances, the replacement with synthetic products of edible fats used in technology, and several others. Work on the solution of problems pertaining to the subjects mentioned above is becoming increasingly important in plans of scientific research.

In addition to the activities outlined above, the institutes and members of the department participate in investigations conducted by other departments of the Academy of Sciences USSR on a number of major problems, including the problem of the chemical conversion of hydrocarbons into the basic products of the heavy organic synthetic industry, development of the production and utilization of rare elements, etc.



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The efforts made by the institutes are concentrated on the solution of these problems and of equally important problems.

During the discussion of Dubinin's reports, the participants at the meeting emphasized the importance of reinforcing the efforts made along some of the lines mentioned in that report. Some of the problems connected with the plan for research work, the training of personnel, and the application of the results of the work were defined more precisely during the discussion. The importance of strengthening the contacts with industry and with industrial experimental organizations to secure an early technological evaluation of the results of scientific work was emphasized.

Academician S. I. Vol'fkovich stated that the principal criterion to be applied in evaluating the activity of the department is production of results which are applicable from the theoretical, methodological, and practical standpoints. The institutes of the academy must solve in principle the problems set by industry and then transfer the results obtained by them to the specialized branch institutes, where the work will be continued with the collaboration of the scientists of the academy acting as consultants.

In a number of statements that were made (those of Academicians A. P. Vinogradov and A. A. Semenov and of Corresponding Members of the Academy I. P. Alimarin and N. I. Shuykin), the problem of planning the work of scientists was discussed.

B. V. Deryagin, Corresponding Member of the Academy of Sciences USSR, said that the activity of an individual scientist or of a whole institute must be considered in connection with analogous work being done in the same field in the USSR and abroad. Only by doing this can one determine the significance of the work under consideration. In order to give extensive information on investigations which have been completed or are being conducted, one must emphasize to a greater extent the presentation of scientific reports at sessions of the department and show more temerity in expanding scientific discussions on the most acute problems.

In connection with the problem of the quality of scientific investigations, N. P. Luzhnaya, Doctor of Chemical Sciences, broached the question in regard to the ideological work done at the institutes, an activity the status of which is reflected both in the subject matter of the investigations and in their scientific level. She proposed an expansion of the practice of holding methodological seminars as a measure which will raise the ideological level of scientific investigations.

In his concluding remarks Dubinin defined with greater precision some aspects of the activity of the Department of Chemical Sciences with respect to the coordination of its work with that of other departments when overlapping problems or borderine problems are involved, in regard to professional solidarity in connection with the work, concerning the equipment of laboratories, etc.

The general meeting approved the work done by the Bureau of the Department in 1954 and recommended that the bureau take into account in its further activity the suggestions made during the meeting.

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